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H01M 4/38**H01M 4/02****H01M 10/40**(21)Application number : **08-240729**(71)Applicant : **MITSUBISHI CABLE IND LTD**(22)Date of filing : **11.09.1996**(72)Inventor : **MARUMOTO MITSUHIRO
TAKADA YOSHINORI****(54) LITHIUM SECONDARY BATTERY NEGATIVE ELECTRODE AND LITHIUM SECONDARY BATTERY USING IT**

(57)Abstract:

PROBLEM TO BE SOLVED: To eliminate an internal short-circuit, and maintain a function as negative electrode active material by using aluminum powder having conductive inorganic coating layers on the surfaces thereof as the negative electrode active material.

SOLUTION: By forming conductive inorganic coating layers on the surfaces of aluminum powder, in a coating layer forming process, one part of or the most part of ready made aluminum oxide on the surfaces of the aluminum powder is removed, and after the formation of the coating layers, the new producing of the aluminum oxide is suppressed. Thereby, the aluminum powder maintains initial mechanical rigidity, and deals with a pulverization issue resulting from the repeated charge and discharge of a secondary battery so as to improve the same. As an aluminum simple substance, the same of purity of 99 percentage by weight or more is preferable, and the purity of 99.9 percentage by weight or more is particularly preferable.

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CLAIMS

[Claim(s)]

[Claim 1] The negative electrode for lithium secondary batteries characterized by using for a front face the aluminum system powder which has a conductive inorganic enveloping layer as a negative-electrode active material.

[Claim 2] The negative electrode for lithium secondary batteries according to claim 1 which is at least one sort as which aluminum system powder was chosen out of the group which consists of aluminum and an aluminium alloy.

[Claim 3] The negative electrode for lithium secondary batteries according to claim 1 or 2 which is at least one sort chosen out of the group which the component of a conductive inorganic enveloping layer becomes from Sn, Zn, In, Pb, Mn, Mo, Co, Cu, Fe, nickel, two or more sorts of those alloys, Sn oxide, and In oxide.

[Claim 4] The lithium secondary battery characterized by the potential difference with the negative electrode for lithium secondary batteries according to claim 1 to 3 and this negative electrode consisting of the positive electrode which has the positive active material which is 1V at least and nonaqueous electrolyte which has lithium salt, or a lithium ion conductivity solid electrolyte.

[Claim 5] The lithium secondary battery according to claim 4 whose positive active material is a lithium inclusion transition-metals oxide.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the lithium secondary battery which used the negative electrode for lithium secondary batteries, and it.

[0002]

[Description of the Prior Art] There is a problem in which a dendrite is produced by charge and the internal shunt is caused as a negative-electrode active material for lithium secondary batteries when the negative-electrode active material of such a lithium system is used, although a metal lithium and various kinds of lithium alloys were common conventionally. Furthermore, although the negative-electrode active material of a lithium system is used with tabular [of one sheet], while repeating the charge and discharge of a rechargeable battery, there is also a problem which this negative-electrode active material carries out the pulverization gradually within a short period of time comparatively, and loses the function. On the other hand, although using carbon as a negative-electrode active material instead of the negative-electrode active material of a lithium system is also performed, this negative-electrode active material has the problem whose capacity per unit volume is not enough.

[0003] There is a proposal which uses aluminum system powder as a negative-electrode active material. There is also the advantage which the reacting weight of the lithium per unit surface area becomes relatively and low since the surface area per unit weight is as large as several times to several 100 times of that of the negative-electrode active material of a lithium system since the capacity per unit volume is large since the capacity that aluminum system powder generally carries out the occlusion exudation of the lithium is large, and it is moreover powder, and a dendrite seldom produces as a result. However, the lithium secondary battery which used the negative-electrode active material of aluminum system powder has the problem to which the internal resistance of a cell increases gradually while in use by the raw Narimasu size of the amount of aluminum oxides in an aluminum system powder front face with time, and electromotive force falls. It destroys, while a rechargeable battery repeats charge and discharge, and the aluminum system powder which became brittle by furthermore generating an aluminum oxide is flour-ized further, and also has the problem which secedes from a negative electrode and loses the function.

[0004]

[Problem(s) to be Solved by the Invention] The technical problem of this invention is to offer the lithium secondary battery using the negative electrode for lithium secondary batteries and it which consist of a negative-electrode active material of the aluminum system powder with which the problem of internal resistance increase of a lithium secondary battery and the problem of the above-mentioned flour-izing have been improved.

[0005]

[Means for Solving the Problem] this invention has the following characteristic feature.

1. Negative electrode for lithium secondary batteries characterized by using for front face aluminum system powder which has conductive inorganic enveloping layer as negative-electrode active material.
2. Negative electrode for lithium secondary batteries of one above-mentioned publication which is at least one sort as which aluminum system powder was chosen out of group which consists of aluminum and aluminium alloy.
3. Negative electrode for lithium secondary batteries the above 1 which is at least one sort chosen out of group which component of conductive inorganic enveloping layer becomes from Sn, Zn, In, Pb, Mn, Mo, Co, Cu, Fe, nickel, two or more sorts of those alloys, Sn oxide, and In oxide, or given in two.
4. Lithium secondary battery characterized by the potential difference with negative electrode for lithium secondary batteries of publication and this negative electrode becoming either of the above 1-3 from positive electrode which has positive active material which is 1V at least and nonaqueous electrolyte which has lithium salt, or lithium ion conductivity solid electrolyte.
5. Lithium secondary battery of four above-mentioned publication whose positive active material is lithium inclusion transition-metals oxide.

[0006]

[Function] By forming a conductive inorganic enveloping layer in the front face of aluminum system powder, the technical problem of the above-mentioned this invention is solved by the ground described below. That is, in the process which forms this enveloping layer, most aluminum most [established / established parts or] on an aluminum system powder front face are removed, it sets after formation of this enveloping layer, and new generation of an aluminum oxide is suppressed or prevented by this enveloping layer. Moreover, for the reason, the flour-ized problem based on the charge and discharge by which aluminum system powder holds early mechanical robustness, and a rechargeable battery is repeated is also improved.

[0007]

[Embodiments of the Invention] In this invention, aluminum system powder may be powder, such as an aluminum simple substance and an aluminium alloy. Especially as an aluminum simple substance, the thing of 99.9 % of the weight or more of purity is [99 % of the weight or more of purity] desirable. An aluminum-M system alloy is illustrated as an aluminium alloy. M in this aluminum-M system alloy is a kind or two sorts or more of alloy contents chosen out of Si, Zn, In, Ag, Te, Mg, Pb, Bi, Sn, etc., and aluminum:M (weight ratio) is 30:70-99:1, and a thing that is especially 50:50-80:20. 0.1-50 micrometers of the mean particle diameters of these aluminum system powder are 5-20 micrometers preferably. At least one sort of the above-mentioned aluminum simple substance powder, at least one sort of aluminium alloy powder, or the mixture powder of an aluminum simple substance and an aluminium alloy is used, and the mixture powder of 1:9-3:7 has an especially desirable aluminum simple substance:aluminium alloy (weight ratio).

[0008] As a component of a conductive inorganic enveloping layer, it sets to the conductivity usually required of the negative electrode for lithium secondary batteries, for example, a room temperature, and is at least 1×10^4 . The metal alloyed with various kinds of metals possessing the conductivity of omegam-1, an alloy, a metallic oxide, or a lithium is mentioned. As a metal alloyed with a lithium, Sn, Zn, In, Pb, Cu, etc. are illustrated and they also make the operation which alloys with the lithium separated on the front face of aluminum system powder at the time of charge other than elimination of an aluminum oxide, or a generation prevention operation, diffuses a lithium inside aluminum system powder, and prevents detailed-ization of this powder. A lithium and the metal of non-reactivity, for example, Mn, Mo, Co, Cu, Fe, nickel, etc., form an enveloping layer by itself, and they act elimination and generation prevention of an aluminum oxide. As an alloy for covering, Ag-Cu, Ag-In, Pb-Sn, Ag-Mn-Sn, etc. have a diffusion coefficient close to the diffusion coefficient of the lithium in the inside of aluminum in this alloy for covering of a lithium, for example, or the thing beyond it is desirable. Moreover, since these very thing is conductivity, Sn and the oxide of In may be formed by performing oxidation treatment suitable after forming Sn and the layer of In.

[0009] A conductive inorganic enveloping layer can be formed by an electroless deposition method, the electroplating method, the self-possessed method, the vacuum deposition, or the other technique. In an electroless deposition method or an electroplating method, since alkaline plating liquid is usually used, the lysis elimination of the aluminum oxide of an aluminum system powder front face is carried out by the alkalinity of this plating liquid at the time of plating. In a self-possessed method or a vacuum deposition, an aluminum oxide is removed by the energy at the time of the deposition of a conductive inorganic lagging material, or vacuum evaporatio, and, instead, this inorganic lagging material is covered. It is desirable to be referred to as about at least 0.05 micrometers, and when thickness of a conductive inorganic enveloping layer is especially set to about 0.1-1 micrometer, it is much more desirable.

[0010] Let the negative-electrode active material of the aluminum system powder which has a conductive inorganic enveloping layer on a front face be a negative electrode for lithium secondary batteries by usual technique with a usual binder. A polytetrafluoroethylene, a poly-vinylidene fluoride, polyethylene, etc. are illustrated as a binder. the mixing ratio with the aluminium system powder which has a Binder:conductivity inorganic enveloping layer -- 1:99-20:80 -- it is 5:95-15:85 preferably

[0011] The lithium secondary battery of this invention consists of nonaqueous electrolyte of the above-mentioned negative electrode for lithium secondary batteries, the positive electrode which has a positive active material and a liquid, or a solid-state. That whose potential difference with this negative electrode is 1V at least as a positive active material, For example, V2 O5, MnO2, LiMn2 O4, and LiCoO2, LiNi0.5 Co0.5 O2, LiNiO2, and a Li-Co-P system multiple oxide (LiCo0.5 P0.5 O2 --) LiCo0.4 P0.6 O2, LiCo0.6 P0.4 O2, LiCo0.3 nickel0.3 P0.4O2, and LiCo0.2 nickel0.2 P0.6 O2 etc. -- lithium inclusion transition-metals oxides, such as TiS2, MoS2, and MoO3, are desirable Also among these, especially the Li-Co-P system multiple oxide that can make high especially the electromotive force and charge and discharge voltage of a rechargeable battery is desirable.

[0012] As nonaqueous electrolyte, the electrolytic solution and the solid electrolyte which melted salts in the organic solvent can be used. As salts used for the electrolytic solution, LiClO4, LiBF4, LiPF6, LiAsF6, LiAlCl4, Li(CF3 SO2)2 N, etc. are illustrated, and those kinds or two sorts or more of mixture is used. As an organic solvent, ethylene carbonate, propylene carbonate, dimethyl sulfoxide, a sulfo run, gamma-butyrolactone, 1, 2-dimethoxyethane, N.N-dimethylformamide, a tetrahydrofuran, 1, 3-dioxolane, 2-methyl tetrahydrofuran, diethylether, etc. are illustrated, and those kinds or two sorts or more of mixture is used. Moreover, the concentration of the above-mentioned salts in the electrolytic solution is used by melting by the concentration of about 0.1-3 mols/l. That with which a kind of the above-mentioned salts or two sorts or more were mixed by a polyethylene oxide, polyphosphazene, a poly-aziridine, polyethylene sulfides or each of those derivatives, two or more sorts of those mixture, etc. as a solid electrolyte is illustrated. A solid electrolyte serves as the separator between the positive/negative poles of a cell.

[0013]

[Example] Hereafter, an example explains this invention much more in detail, the example of a comparison is shown, and the remarkable effect of this invention is also shown.

[0014] It supplied to the 10 % of the weight aqueous solution of the zinc displacing agent (DI-470 by Nippon Chemical Industrial Co., Ltd.) which held 99.95 % of the weight of example 1 purity, and the aluminium powder of 20 micrometers of mean particle diameters at 4 degrees C, and pulled up after leaving it under stirring for 120 seconds, and the pure water washed, it dried in the vacuum at 80 degrees C for 3 hours, and Zn plating aluminium powder was obtained. When observation measurement of the mean thickness of Zn layer of this plating powder was carried out with the electron microscope, it was 1 micrometer. The negative-electrode active material of Zn plating aluminium powder and the 5 % of the weight N-methyl-2-pyrrolidone solution of a binder slack poly vinylidene fluoride which were obtained in this way were mixed by the

weight ratio of 1:1. Next, this mixed liquor was applied on the copper substrate with a thickness of 15 micrometers, and the negative electrode for lithium secondary batteries which consists of a copper substrate which dries in a vacuum at 120 degrees C for 3 hours, and has a negative-electrode active material layer with a thickness of 30 micrometers on one side was obtained. [0015] 99.95 % of the weight of example 2 purity and the aluminium powder of 20 micrometers of mean particle diameters were supplied to the 10 % of the weight aqueous solution of Sn plating undiluted solution by the high-grade chemistry company held at 5 degrees C after Zn substitute on the same technique and same conditions as an example 1, it pulled up after leaving it under stirring for 120 seconds, and the pure water washed, it dried in the vacuum at 80 degrees C for 3 hours, and Sn plating aluminium powder was obtained. When observation measurement of the mean thickness of Sn layer of this plating powder was carried out with the electron microscope, it was 1 micrometer. The negative electrode for lithium secondary batteries which consists of a copper substrate which has a negative-electrode active material layer with a thickness of 30 micrometers on one side on the same technique and the same conditions as an example 1 was obtained using the negative-electrode active material of Sn plating aluminium powder obtained in this way.

[0016] Instead of the example 3 aluminium powder, aluminium alloy powder with a mean thickness [of Zn deposit] of 1 micrometer was obtained on the same technique and the same conditions as an example 1 except having used the aluminium alloy powder of 17 micrometers of the mean particle diameters of alloy composition of aluminum-12%Si. The negative electrode for lithium secondary batteries which consists of a copper substrate which has a negative-electrode active material layer with a thickness of 30 micrometers on one side on the same technique and the same conditions as an example 1 was obtained using the negative-electrode active material of Zn plating aluminium alloy powder obtained in this way.

[0017] Instead of the example 4 aluminium powder, aluminium alloy powder with a mean thickness [of Sn deposit] of 1 micrometer was obtained on the same technique and the same conditions as an example 2 except having used the aluminium alloy powder of 17 micrometers of the mean particle diameters of alloy composition of aluminum-12%Si. The negative electrode for lithium secondary batteries which consists of a copper substrate which has a negative-electrode active material layer with a thickness of 30 micrometers on one side on the same technique and the same conditions as an example 1 was obtained using the negative-electrode active material of Sn plating aluminium alloy powder obtained in this way.

[0018] 99.95 % of the weight of example 5 purity and the aluminium powder of 20 micrometers of mean particle diameters were held at 70 degrees C after Zn substitute on the same technique and same conditions as an example 1, and it supplied to the 10 % of the weight aqueous solution of a silver electroless deposition undiluted solution after that, and pulled up after leaving it under stirring for 120 seconds, and the pure water washed, it dried in the vacuum at 80 degrees C for 3 hours, and Ag plating aluminium powder was obtained. When observation measurement of the mean thickness of Zn layer of this plating powder was carried out with the electron microscope, it was 1 micrometer. The negative-electrode active material of Ag plating aluminium powder and the 5 % of the weight N-methyl-2-pyrrolidone solution of a binder slack poly vinylidene fluoride which were obtained in this way were mixed by the weight ratio of 1:1. Next, this mixed liquor was applied on the copper substrate with a thickness of 15 micrometers, and the negative electrode for lithium secondary batteries which consists of a copper substrate which dries in a vacuum at 120 degrees C for 3 hours, and has a negative-electrode active material layer with a thickness of 30 micrometers on one side was obtained.

[0019] Instead of the example 6 aluminium powder, aluminium alloy powder with a mean thickness [of Ag deposit] of 1 micrometer was obtained on the same technique and the same conditions as an example 6 except having used the aluminium alloy powder of 17 micrometers of the mean particle diameters of alloy composition of aluminum-12%Si. The negative electrode for lithium secondary batteries which consists of a copper substrate which has a negative-electrode active material layer with a thickness of 30 micrometers on one side on the same technique and the same conditions as an example 6 was obtained using the negative-electrode active material of Zn plating aluminium alloy powder obtained in this way.

[0020] It used as a negative-electrode active material, without carrying out plating processing of the aluminium powder used in the example of comparison 1 example 1, and the negative electrode for lithium secondary batteries which consists of a copper substrate which has a negative-electrode active material layer with a thickness of 30 micrometers on one side on the same technique and the same conditions as an example 1 was obtained.

[0021] It used as a negative-electrode active material, without carrying out plating processing of the aluminium alloy powder used in the example of comparison 2 example 2, and the negative electrode for lithium secondary batteries which consists of a copper substrate which has a negative-electrode active material layer with a thickness of 30 micrometers on one side on the same technique and the same conditions as an example 1 was obtained.

[0022] LiNiO₂ of 30 micrometers of the mean particle diameters as three to examples 7-12 and example of comparison 4 positive active material, The scale-like carbon as an electric conduction agent and the 5 % of the weight N-methyl-2-pyrrolidone solution of a binder slack poly vinylidene fluoride are mixed by the weight ratio of 9:1:9. The obtained mixed liquor was applied on the aluminum substrate with a thickness of 25 micrometers, and the positive electrode for lithium cells which consists of an aluminum substrate which dries in a vacuum at 120 degrees C for 3 hours, and has a positive-active-material layer with a thickness of 80 micrometers on one side was obtained. a disk with a diameter [the negative electrode for lithium cells of the positive electrode for lithium cells obtained in this way, each above-mentioned example, and the example of a comparison to] of 15mm -- obtaining -- between disk-like two poles -- the shape of a disk with a diameter of 19mm -- and a porous polypropylene film with a thickness of 25 micrometers -- pinching -- subsequently -- one mol [per 1l. of mixed solutions of 1:1 volume ratios of propylene carbonate and diethyl carbonate] LiPF₆ It melted, the obtained electrolytic solution was sunk in and the coin type [0023] Number-of-times N of a charge-and-discharge repeat until electric discharge capacity falls to 80% in the early stages of charge and discharge of electric discharge capacity about each of the coin type lithium secondary battery of the examples 7-12

and the examples 3-4 of a comparison was measured. The result is shown in Table 1. this table shows that the lithium secondary battery using the negative electrode for lithium cells of this invention has the longevity life which was markedly alike and was superior to the cell of the example of a comparison

[0024]

[Table 1]

	負極	N (回)
実施例 7	実施例 1	9 6 7
実施例 8	実施例 2	1 0 4 6
実施例 9	実施例 3	1 0 6 0
実施例 10	実施例 4	1 1 9 5
実施例 11	実施例 5	8 5 5
実施例 12	実施例 6	1 0 8 0
比較例 3	比較例 1	8 4
比較例 4	比較例 2	1 1 0

[0025]

[Effect of the Invention] Since the problem of aluminum oxide generation on an aluminum system powder front face which should be hated is improved by forming a conductive inorganic enveloping layer in the front face of aluminum system powder, the advantage of the large capacity which aluminum system powder originally has as a negative-electrode active material, or dendrite-proof nature is harnessed. A deer is carried out and a long lasting thing is obtained from the lithium secondary battery of this invention using the negative electrode for lithium secondary batteries which consists of a negative-electrode active material of the aluminum system powder of this invention.

[Translation done.]